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Synthesis of $MgAl_2O_4$ thin films by Al and Mg anodic evaporation in a low-pressure arc (Ar/O_2, 1 Pa)

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Films of magnesium aluminate spinel were synthesized by reactive anodic evaporation of Al and Mg in a low-pressure arc (Ar/O_2, 1 Pa) with vapor condensation at low temperature ($\sim 400^\circ$C). Film deposition was assisted by ion flux 25−100 eV, 1−2 mA/cm^2) with a significant content of metal ions. Cubic spinel films had a strong texture (100) and microstrains of the crystal lattice are of $\sim 1\%$. The deposition rate of films was 1−3 μm/h at controlling of a relative content of Al and Mg atoms within 1.2−2.4.

Keywords: anodic evaporation, ionic assistance, magnesium aluminate spinel, self-heating cathode, thin films.

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Magnesium aluminate spinel $MgAl_2O_4$ (MAS) has high chemical and thermal resistance, high melting point and hardness, transparency in a wide spectral range. Thin films of MAS are promising for use as thermal barrier and buffer layers and reflective optical coatings [1]. Currently, MAS films are mainly produced by chemical reaction-based methods such as chemical vapor deposition, including organometallic chemical vapor deposition, atomic layer deposition, plasma jet deposition, etc. [1]. Physical vapor deposition of MAS films was realized by evaporating [2] or sputtering [3] targets from the solid MAS. In experiments with reactive sputtering of pure metals Al and Mg in a dual magnetron, the deposited films changed from crystalline (MgO) to amorphous state with increasing aluminum concentration [4]. The energy of atoms on the film surface at a temperature of 500 K did not provide overcoming the activation barrier of the spinel formation reaction, so the increase in the concentration of aluminum atoms led to an increase in the concentration of vacancies and amorphization of MgO films.

It is known that the crystallization temperature of films, including oxide films, can be reduced by ion bombardment, which increases the energy of atoms on the surface of the growing coating and increases their diffusive mobility [5]. Thus, in [6] it was shown that bombarding the surface of a growing aluminum oxide film with flow of ions with energy up to 100 eV and current density up to 20 mA/cm^2 leads to a decrease in the temperature of formation of α-Al_2O_3 in the film, deposited by reactive thermal evaporation of Al to 500−550°C, whereas under equilibrium conditions the temperature of transformation of γ-Al_2O_3 into α-phase is in the range 850−1050°C, and the transition is fully completed at 1200−1300°C.

The aim of the present work is to obtain crystalline MAS by separate evaporation of Al and Mg in a low-pressure arc discharge with a self-heated hollow cathode. Such a discharge is able to function for a long time in the mode of oxygen plasma generation, and also provides an opportunity to regulate in wide limits the intensity of ion assistance and the rate of film deposition [7].

The diagram of the experimental setup is shown in Fig. 1. The current with the self-heated hollow cathode discharge *1* is closed to two crucibles *2*, *3* having an anodic potential, and a rod-type anode *4*. The heating power of graphite anode electrodes is determined by the values of the discharge current and anodic potential drop. By changing the currents in the circuits of crucibles in which Al and Mg are separately loaded, the rate of vaporization of each of the metals is controlled. The magnitude of the current in the rod-type anode circuit affects the plasma density and consequently the ion assistance current density. The temperature of the samples *5* depends on the intensity of the ion accompaniment and is controlled by a radiation heater *6*.

The main difficulty in forming a flow of aluminum and magnesium vapors, the ratio of partial pressures of metal vapors in which provides the required composition of the deposited films, is that, despite the close values of the melting point of Al (660.4°C) and Mg (650°C), their saturated vapor pressure at the same temperatures differ by several orders of magnitude [8]. Therefore, to obtain a partial vapor pressure of these metals ~ 10 Pa, at which an acceptable film deposition rate is provided, it is necessary to heat Mg to a temperature of the order of 500°C, whereas Al requires a temperature of ~ 1350°C. However, during reactive evaporation of Mg from the solid state, an oxide film forms on its surface, which blocks evaporation. Reducing the aperture size of the Mg-crubicle and increasing the current in the crucible circuit, on the outer surface of which a non-conductive oxide film is formed, made it possible to realize the mode of evaporation of Mg from the melt and reduce the oxygen flow inside the crucible, which ensured stable magnesium

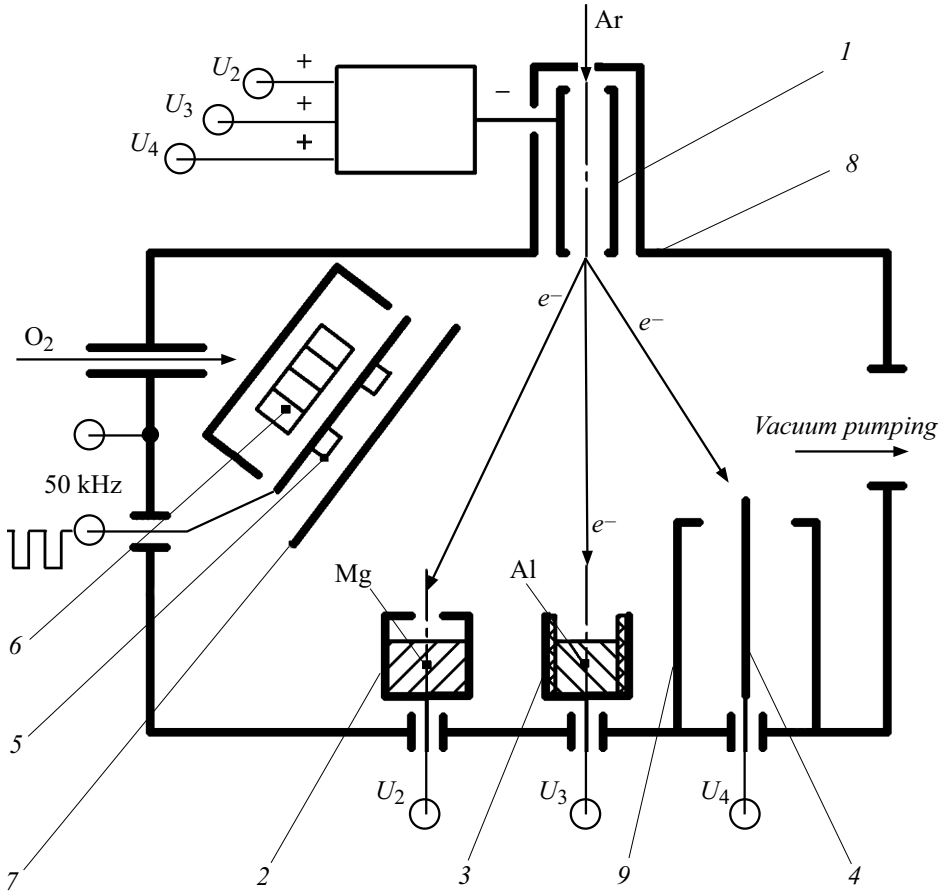

Figure 1. Schematic diagram of thin film deposition setup $MgAl_2O_4$: self-pumped cathode (*1*), crucibles (*2*, *3*), rod-type anode (*4*), samples (*5*), heater (*6*), shutter (*7*), vacuum chamber (*8*), screen (*9*).

evaporation. The interaction of aluminum with carbon in the process of evaporation of Al from the graphite crucible at temperatures above 1200°C leads to the formation of aluminum carbide [9] on the crucible walls, which, unlike graphite, is wetted by aluminum. This promotes the escape of the liquid Al film to the outer surface of the crucible. Shielding the inner wall of the crucible with a ceramic tube enabled elimination of this source of instability in the aluminum evaporation process.

The discharge system with self-heated cathode and vaporized anode is stable in the oxide deposition mode when Ar (100 sccm) is fed through the cathode cavity and O_2 (35 sccm) is injected into the volume. The appearance of metal vapors leads to a decrease in the arc burning voltage. Thus, when magnesium is vaporized in an arc with a current of 2 A, the voltage decreases from 80 to 54 V. The high temperature (~ 1000°C) of the rod-type anode provides rapid re-evaporation of metal atoms, which prevents the formation of oxide films on the anode, hindering the burning of the discharge. At the same time, due to the low partial pressure of carbon in the volume, its possible impurity in the films is less than the lower limit of detection by energy-dispersive spectroscopy.

After the crucibles were loaded and the substrates were mounted, the chamber was evacuated by a turbomolecular pump to a pressure of 10^{-3} Pa, then argon was fed through the cathode cavity and a discharge was ignited on the rod-type anode (20 A, 50 kHz, 10 μs), a negative pulse bias voltage was applied to the sample holder (-500 V, 50 kHz, 10 μs), and the substrate surface was cleaned by ion sputtering. When using Si(100) single crystal silicon substrates with a buffer layer of thin SiO_2, sample preparation was limited to cleaning in an ultrasonic solvent bath, and ionic treatment was not performed. Then oxygen was supplied to the chamber volume and heating currents were set in the crucible circuits. When the crucible temperature reached steady-state values, the bias voltage ($25-100$ V) was set, the screen was opened, and the substrate temperature was corrected by changing the external heating power. The metal content in the vapor stream was monitored by measuring the amplitude of excited atom lines of Al (394.4 nm) and Mg (517.3 nm) in the plasma emission spectrum. The ratio of line amplitudes at which the stoichiometric composition of MAS is ensured was determined in preliminary experiments. The phase and elemental composition of the films were analyzed by X-ray diffraction and scanning electron microscopy (SEM).

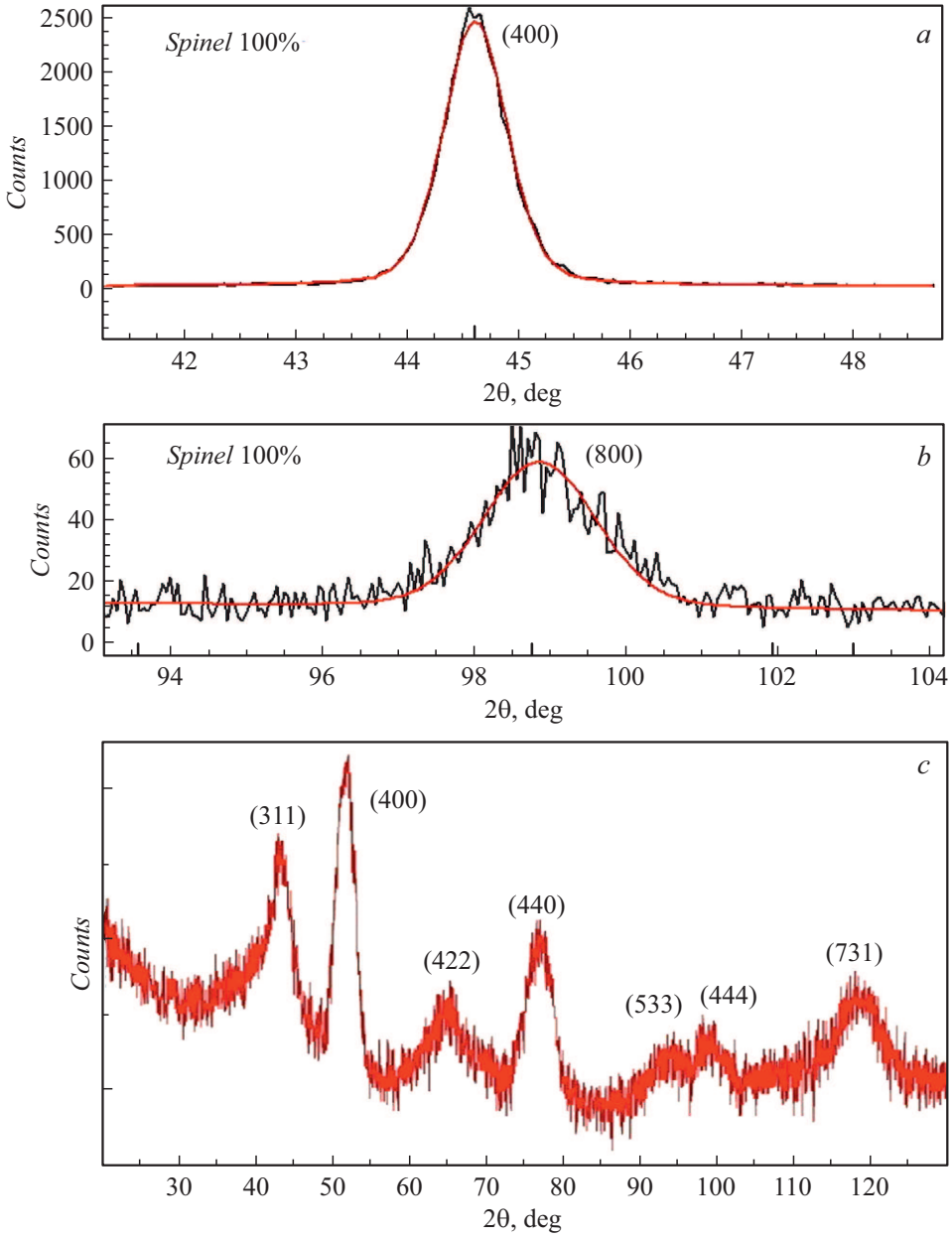

Figure 2. X-ray diffraction patterns of MAS film on Si substrate obtained in $\theta-2\theta$ line-scan mode (400) (*a*) and (800) (*b*) and in 5° sliding beam incidence mode (*c*).

Films deposited at low temperatures (250°C) contained a single crystalline phase (MgO). The MAS phase was formed at temperatures above 400°C under ion assistance conditions ($1-2\,mA/sm^2$, $25-100\,eV$), without which amorphous films were formed at temperatures up to 600°C, annealing of which in atmosphere (2 h, 800°C) did not lead to the formation of MAS.

Diffraction patterns of MAS film deposited on $Si(100)/SiO_2$ substrate at temperature 400°C and bias voltage $-25\,V$, were obtained in the standard $\theta-2\theta$-scanning mode on a D8 DISCOVER diffractometer at copper radiation ($CuK_{\alpha 1,2}$). The diffraction patterns contain a Si(400) line and cubic MAS lines located at $2\theta = 44.61°$ (400) and 98.76° (800), which are shifted toward smaller angles relative to the tabulated values of 44.833 and 99.347°, respectively (JCPDS pdf 00-021-1152) (Fig. 2, *a*, *b*). Processing of diffraction patterns was performed using the TOPAS 3 program. The obtained results indicate the formation of a highly textured film with a high degree of microstrain of the MAS lattice, the level of microstrain of which amounted to 1.3%, the size of the coherent scattering region was 51 nm, the lattice period was $a = 0.8122\,nm$, while the tabular value was $a = 0.80831\,nm$. Numerous signals from polycrystalline spinel (Fig. 2, *c*) were detected on a Pananalitical Empyrean diffractometer on cobalt radiation in parallel beam geometry

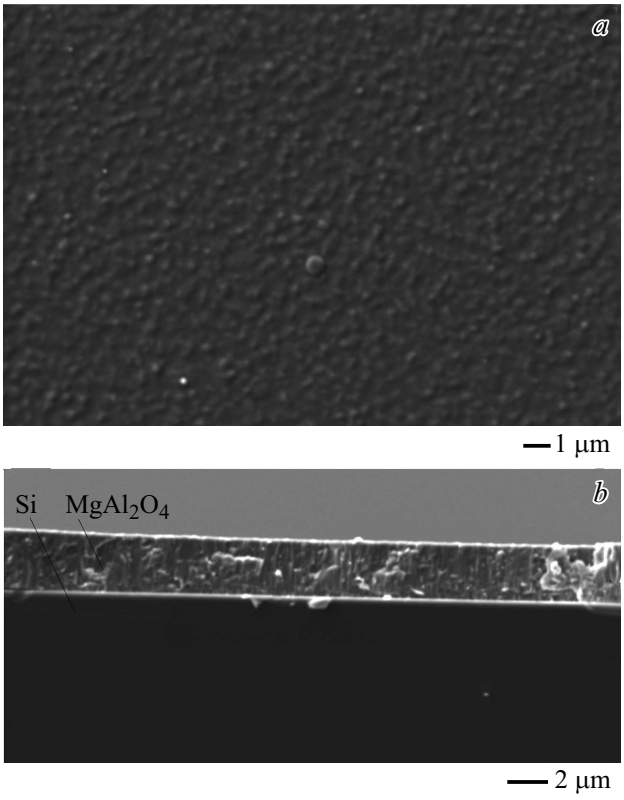

Figure 3. SEM images of the surface (a) and cross section (b) of the film $MgAl_2O_4$.

in the sliding beam incidence mode at an angle of 5°. Note that the appearance of strong texture of films under low-temperature crystallization conditions under the action of ion bombardment was observed by us earlier in the synthesis of α-aluminum oxide films [6].

Fig. 3 shows images of the surface of the MAS film and its cross section obtained by the method. An EVO LS 10 Carl Zeiss NTS scanning electron microscope was used. The film has a dense columnar structure. The thickness of the film deposited during 1 h was $2.9 \pm 0.2\,\mu$m. The film density estimated from the sample mass change and film thickness was $3.6 \pm 0.1\,g/cm^3$, which is close to the known data for stoichiometric spinel ($3.58\,g/cm^3$) [1]. The elemental composition of the film measured by energy-dispersive X-ray technique is characterized by the ratio Mg:Al:O=16.79:22.89:60.32 (at.%), and excess Mg did not lead to the separation of the second phase.

It is preliminarily found that films with MAS structure and atomic ratio Al:Mg > 2 are formed at temperatures greater than 400°C under ion bombardment conditions when the aluminum flux is increased relative to the stoichiometric flux. When the magnesium vapor flux was increased significantly above the stoichiometric flux, two-phase films were formed with at approximately the same content of phases $MgAl_2O_4$ and MgO, the appearance of texture with dominance of closely spaced spinel lines (400) at $2\theta = 43.45°$ ($CuK_{\alpha 1,2}$) and MgO (100) at $2\theta = 42.85°$ ($CuK_{\alpha 1,2}$) was observed. The influence of the ratio of Mg and Al in the vapor flow on the phase composition, microstructure and properties of the resulting films will be the subject of a separate study.

The microhardness H_v of the films was measured using a DUH-211/211S dynamic ultramicrohardness tester (Shimadzu) at an indenter penetration depth equal to 0.1 of the film thickness. The microhardness value H_v of the films depended on their elemental and phase composition. For single-phase MAS films, the value of H_v was typically 13–15 GPa. Films with a significant excess of magnesium had microhardness not more than 8 GPa, which is close to the values H_v for periclase MgO. The microhardness of the film shown in Fig. 3 with high microstress level (1.3%) was in the range of 17–25 GPa. As the ion energy increased from 25 to 100 eV, the area of delaminations increased, indicating the growth of internal stresses in the film.

Thus, by separate metal evaporation in Ar/O_2 low-pressure arc at deposition temperature above 400°C with ionic assistance (25–100 eV, 1–2 mA/cm^2), cubic magnesium aluminate spinel films having a dense columnar structure were synthesized. The method of separate evaporation allows the relative content of Al and Mg in spinel films to be adjusted within a wide range. It was the intensive ionic assistance that ensured the formation of the spinel structure in the films obtained by reactive evaporation, at comparable values of temperature and film deposition rate in our experiments and in the system with magnetron sputtering [4] (400°C, 3 μm/h and 500 K, 6 μm/h, respectively).

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Conflict of interest

The authors declare that they have no conflict of interest.

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